

## Evaluation of Pistachio Nuts Stability at Various Conditions Based on Metrohm Rancimat

N. Sedaghat

Department of Food Science, Ferdowsi University of Mashhad (FUM), Mashhad, Iran

**Abstract:** The pistachio nuts are one of the favorite tree nuts of the world. Iran is one of the world's most important areas for the production of this nut, the Ohadee variety of Iranian raw dry pistachio nuts was selected for the experiments. The method of Accelerated Shelf Life Testing (ASLT) used for storage of pistachio. Peroxide value (PV), Free Fatty Acid(FFA) and Induction Time(IT) of raw dried pistachio nuts were investigated at 21%, 8% & < 2% O<sub>2</sub> and different storage temperature (5, 20, 35 and 45°C). Samples were experimented at 4,6,8,10 and 12 weeks by use of split-plot design. Results showed that the Induction Time under factors of temperature and storage time were high significant (p< 0.01) but under factor of O<sub>2</sub> % was significant (p<0.05) and optimum storage condition for raw dried pistachio nuts determined at 20°C and < 2% O<sub>2</sub> based on Induction Time (IT).

**Key words:** Pistachio nuts • ASLT • Rancimat • Induction time

### INTRODUCTION

The pistachio (*Pistacia vera L.*), known as green gold due to its high economical value, is one of the deciduous and popular nuts in the world. The global pistachio production volume increases steadily, estimated by FAO as 489,000Mt in 2005 having risen from 191,000Mt in the 1985. The elevation in the global production is probably due to its good nutritional properties and the reports on its health promoting effects. The kernels are a rich source of oil (50-60 %) and contain linolenic and linoleic fatty acids, essential for human diet and oleic acid. They are highly nutritious and are eaten raw or fried with pepper and salt and form a popular dessert in the Orient and Europe. They are used as a flavoring in cookery and confectionery and also favored, because of the deep green colors of their kernels, in the ice cream and pastry industries [1-2].

Oxidative rancidity is the most important type of fat spoilage because all edible fats, such as components of foods, contain unsaturated triglycerides. Oxidative deterioration of fat results in the development of a pungent offensive off-flavor and the destruction of vitamins (A,D,E,K&C), essential fatty acids, chlorophylls, carotenes, amino acids, proteins, or enzymes by the production of toxic or physiologically active compounds. One of the factors that affect the autoxidation of common

food fats is the total number of unsaturated linkages in the sample. However, the total amount of unsaturation may not be as important as the degree of unsaturation within a given molecule. A fat high in linoleic or linolenic acid would be more susceptible to oxidation than one containing a similar amount of oleic acid. Oxygen is necessary for autoxidation of fats. Therefore, the removal of atmospheric oxygen from a fat or food product exerts a protective effect. Reduction of oxygen levels by nitrogen flushing or vacuum packaging has been used commercially for freeze dried products, ground coffee, roasted nuts, powdered whole milk and dehydrated potato flakes [3-4].

The Metrohm Rancimat recently developed as a rapid automated method. This method allow the determination of the induction time, which is the time before rapid deterioration of the fat or food product and it was shown correlated well with stability under ambient storage condition for a wide range of edible vegetable oils [5]. Some studies have recently been published on the pistachio such as Optimization of the pistachio nut roasting process. Fatty acid oxidation of pistachio nuts stored under various atmospheric conditions and different temperatures. Studies related to the description and evaluation of pistachio nuts quality. Behavior of oil seeds under various storage conditions. Supercritical CO<sub>2</sub> extraction of lipids from roasted pistachio nuts [1-2, 6-8].

Although the chemical composition and oil characteristics of pistachio nuts has been studied extensively, the Induction Time of oil characteristics and use of Rancimat Test for loss of quality in pistachio nuts have not. The objectives of this investigation will be shown the effect of factors such as oxygen, temperature and storage time on the quality of pistachio nuts by Rancimat Test.

## **MATERIALS AND METHODS**

### **Materials**

**Pistachio Nuts Samples:** The Ohadee variety of Iranian pistachio nut was used for the experiments. The raw dry pistachio nut samples with an average moisture content of about 5 % (wet bases) initially were supplied from Rafsanjan Pistachio Factory in Iran. Upon receiving, they were placed in sealed plastic bags and held at 32°F for experiments.

### **Methods**

**Experimental Design and Storage:** One glass container was assigned to each of the combination of three variables studies: (1) Oxygen concentration: 21% (air), 8% and < 2% with nitrogen flushed atmosphere; (2) storage temperature: 5,20,35,45°C; (3) storage time 4,6,8,10,12 weeks. Each glass had two valves and after nitrogen flushing from one valve, air atmosphere go out from another valve and amount of O<sub>2</sub> concentration remained control with Oxygen Analyzer (GFG Company). Total of 600 g of the selected pistachio nuts was placed in each of the 60 jars (4\*3\*5). Aluminum foil was used to cover all jars to exclude light.

**Extraction of Pistachio Nuts Oil:** At appropriate time pistachio nuts were removed from storage and 300 g nuts removed their shells and them were chopped to granule. To accurately report lipid composition, it is important that the lipids be extracted quantitatively without decomposition from the food product. Oil was extracted by 250 ml hexane in a dark place at ambient temperature for Rancimat Test, PV, FFA analysis, the solvent was evaporated under vacuum at 30°C to dryness.

**Instrumental and Chemical Analysis:** The model 743 Rancimat (Metrohm) equipped with an electric heating block was used without modification. Air flow rates were set at 15 L/h and temperature was set at 150°C for all determinations. Glass reaction and air delivery tubes

were scrupulously cleaned by boiling with sodium hydroxide solution(2% w/w)for one hour, followed by cooling and soaking in concentrated hydrochloric acid. The acid was washed off and the tubes were rinsed with distilled water. Peroxide Value (PV) was determined by the Idometric Titration Method according to the method described in Pearson's chemical analysis of foods. Free Fatty Acid (FFA) was determined by Titration Method of AOAC [9-10] as percent oleic acid. All determinations of Induction Time, free fatty acid and peroxide value were performed in duplicate.

**Statistical Analysis:** The results were compared by multifactor analysis of variance (multifactor ANOVA) to test for significant differences. Means of the groups were compared using the least significant difference (LSD) multiple range test by using a Statgraphics statistical packet (Statgraphics plus, 2000). Differences among sample means were reported to be significant when  $p < 0.05$  and SlideWrite 2.0 soft ware used for drawing plots.

## **RESULT AND DISCUSSION**

Pistachio nuts contains around 23% protein, 19% carbohydrate and 5% moisture, it also contains high amounts of K and P and various amounts of Ca, Mg and Fe. The fatty acid composition of the nut is 54.4–71.8% oleic acid, 16.7–35.3% linoleic acid, 7.2–10.5% palmitic acid, 0.9–2.5% stearic acid and less than 2 % linolenic acid. Rancidity, the development of off – flavor which makes a food unacceptable for the consumer, is generally a major problem in nuts during storage. Deterioration in the quality of pistachio nuts during storage is also attributable to lipid oxidation. Oxygen is the main culprit when oxygen in the air reacts with unsaturated fat through a process called autoxidation various break down products are formed which can cause off –flavors. Factors influencing lipid oxidation in addition to the nature of the substrate are free fatty acids, oxygen concentration, temperature, water content, physical condition, fatty acid position, exposure to light, exposure to certain metals, pro-oxidants and antioxidants. The initial oxidation of fat is usually slow and at a relatively uniform rate. This is known as the induction period. At the end of the induction period, when the amount of peroxide formation reaches a certain level, the rate of oxidation accelerates very rapidly. At this point or soon after, the fat begins to smell or taste rancid [11].

Table 1: Analysis of variance (ANOVA) table for the effects of temperature, O<sub>2</sub> % and storage time on Rancimat Induction Time of pistachio nuts

Source	Df	Sum of Squares	Mean Square	F-Ratio
temperature(a)	3	2.10007	0.700024	8.07**
oxygen(b)	2	0.631292	0.315646	3.64*
time(c)	4	10.632	2.65801	30.63**
ab	6	0.393142	0.0655236	0.75ns
ac	12	1.795772	0.149643	1.72ns
bc	8	0.250217	0.0312771	0.36ns
abc	24	0.314717	0.0131132	0.15ns
Residual	60	5.2072	0.0867867	
Total	119	21.3244		

\* : significant (p<0.05) \*\* : high significant (p<0.01) ns : non significant

The Peroxide Value(PV) can't be determined by Idometric Titration methods because of less amount and adsorption of iodine at unsaturated bonds in the fatty acids. However some worker showed it. This difference is due to methods of oil extraction from sample or differences between pistachio varieties. The PV is a good guide to the quality of a fat and a freshly fat should have a PV of less than 1 unit, therefore pistachio nuts can be acceptable in terms of quality [2,12].

The FFA was minimum 0.302% (% Oleic acid) for treatment of 2% O<sub>2</sub>, 5°C, week 4 and maximum 0.755% (% Oleic acid)for treatment of 21 % O<sub>2</sub>, 45°C and week 12(data not shown). In this study the FFA of pistachio nuts is not the same as the value reported by Maskan and Karatas (1998). The difference is due to the differences between pistachio varieties. Since FFA didn't exceed 5 % which is the recommended maximum level in products for human consumption. Pistachio nuts may be acceptable in terms of FFA; similar results were obtained by Maskan and Karatas (1998) during 12 months storage of pistachio nuts under various conditions and evaluation of fatty acid oxidation. He reported that the pistachio nuts had a high stability [2,13].

The Induction Time determination by the Rancimat Test at 150°C. Multiple factor ANOVA results (Table 1) showed that the Induction time under factors of temperature and storage time were high significant (p< 0.01), but under factor of O<sub>2</sub> % was significant (p<0.05) and the interaction of three factors weren't significant (p ≥ 0.05). But LSD Multiple Rang Test revealed that there was no significant difference between some levels of treatments (Figures 1,2 and3).

It is seen from Figure 1 that increase of O<sub>2</sub>% Induction Time(IT) has decreased and the differences in Induction Time value due to the oxygen percent between level of <2% and 21% O<sub>2</sub> was significant(p<0.05), but non significant between levels of 8% O<sub>2</sub> with <2% and 21% O<sub>2</sub>. This results was confirmed that quality of pistachio

nuts under MAP packaging (8% O<sub>2</sub>) with gas flushing (<2% O<sub>2</sub>) and air packaging (21% O<sub>2</sub>) is non significant, Therefore don't introduce use of MAP packaging for pistachio nuts, but gas flushing packaging is useful because it is significant (p<0.05) from air condition (21% O<sub>2</sub>). Blakistone (1998) reported that flushing with N<sub>2</sub> is currently commonly used to reduce residual O<sub>2</sub> in packs containing cashews, pistachios, mixed nuts and dried fruit, it is being successfully used on raw, fried and roasted nuts and alternative to gas flushing is the use of O<sub>2</sub> scavenger systems the use of O<sub>2</sub> scavengers is said to be more effective than gas flushing for reducing the residual O<sub>2</sub> level within containers [4].

From Figure 2, it has been resulted storage of pistachio nuts under 20°C non significant with 5°C and 35°C, it confirmed that for storage of pistachio nuts use of cold storage (5°C) isn't significant. As a consequence we introduce optimum storage condition for raw dried pistachio nuts can be at 20°C and <2% O<sub>2</sub>. High oleic acid content provides the oil with a good stability and a diet very rich in this fatty acid reduces the concentration of cholesterol. A high concentration of oleic acid gave stability to pistachio nuts. Oxidative stability of oleic acid has been studied and reported by many researcher [14-15].

Similar results were obtained by Kader et al(1982), they concluded that pistachio nuts dried to 4-6 % moisture are very stable and could held for up to 12 months at temperature as high as 20°C without significant losses in quality. Maskan and Karatas (1998) reported that differences in peroxide values due to storage conditions were not significantly different during 6 months of storage for pistachio nuts and he showed that the pistachio nuts had a high stability [2,6]. It is seen from Figure 3, the higher of storage time the lower of Induction Time, at the week 12 the IT was 1.143 h and the raw dried pistachio nuts had been an acceptable PV and FFA.

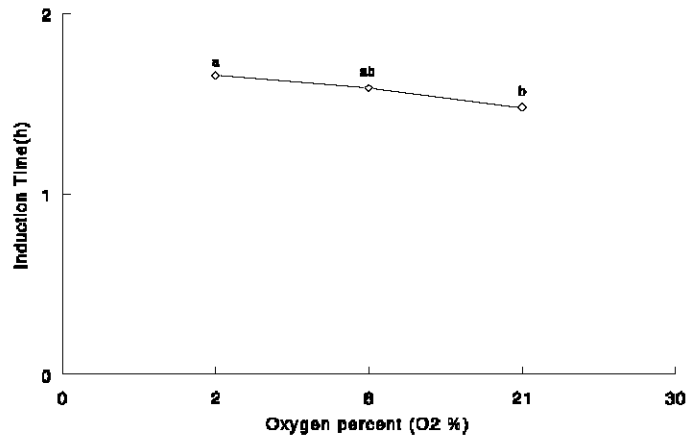


Fig. 1: Multiple Rang tests for Induction Time (IT) at 150°C by Oxygen percent, each point indicates LS mean of 40 determination. Within points, means which share a common letter are not significantly different at  $p < 0.05$  by LSD test

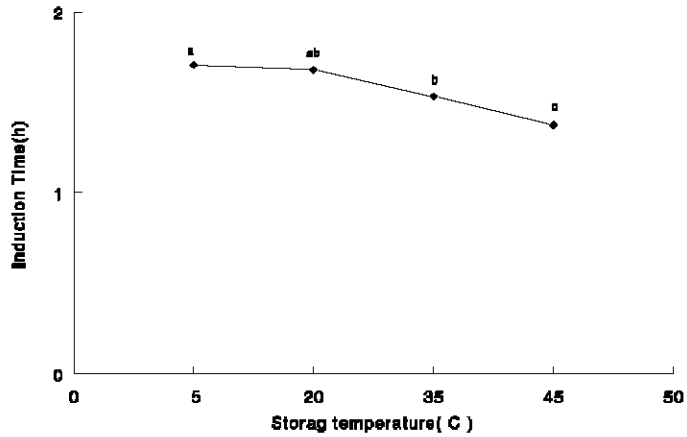


Fig. 2: Multiple Rang tests for Induction Time (IT) at 150°C by Storage temperature, each point indicates LS mean of 30 determination. Within points, means which share a common letter are not significantly different at  $p < 0.05$  by LSD test

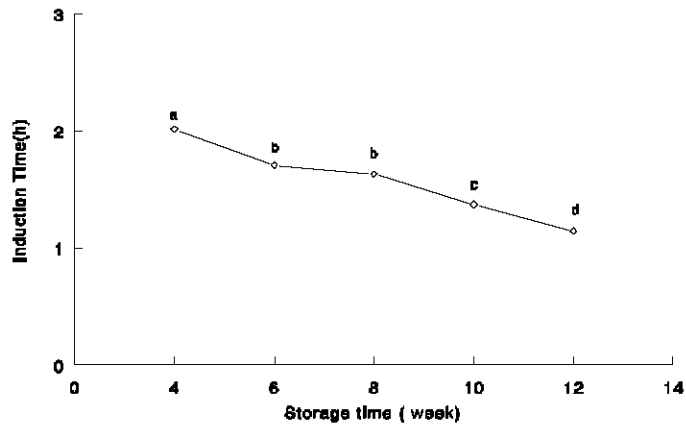


Fig. 3: Multiple Rang tests for Induction Time (IT) at 150°C by Storage time, each point indicates LS mean of 24 determination. Within points, means which share a common letter are not significantly different at  $p < 0.05$  by LSD test

## CONCLUSIONS

According to results, the Peroxide Value (PV) can't be determined by Iodometric Titration methods and the FFA was minimum 0.302% (% Oleic acid) for treatment of 2% O<sub>2</sub>, 5°C, week 4 and maximum 0.755% (% Oleic acid) for treatment of 21 % O<sub>2</sub>, 45°C and week 12. The Induction Time under factors of temperature and storage time were high significant (p< 0.01) but under factor of O<sub>2</sub> % was significant (p<0.05) and optimum storage condition for raw dried pistachio nuts determined at 20°C and < 2% O<sub>2</sub> based on Induction Time (IT).

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